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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

This invention relates to the toner for electrostatic charge image development for developing the electrostatic latent image formed by xerography, an electrostatic recording method, etc. In spite of being established at low temperature, even if it is good, and preservability continues at a long period of time and performs durable printing, especially this invention has good transfer nature, and relates to the toner for electrostatic charge image development without the fall of printing density, or generating of fogging.

[0002]

[Description of the Prior Art]

In image forming devices, such as an electrophotography device and an electrostatic recording device, the electrostatic latent image formed on a photo conductor is first developed by a toner. Subsequently, after the formed toner image is transferred on transfer materials, such as paper, if needed, it is fixed to it by various methods, such as heating, application of pressure, or solvent vapor.

The process that such an image forming device takes a lot of energy is a fixing process.

The thermal pressure fixing method with sufficient energy efficiency is widely used for this fixing.

[0003]

In recent years, the demand to the reduction and improvement in the speed of a running cost in an image forming device is high. In order to meet these demands, what has high efficiency also to a toner is called for, and the toner which has low temperature fixability is proposed as a toner used by said fixing method.

In order to obtain the toner excellent in low temperature fixability, adding petroleum resin to binding resin is already known. For example, the toner with which a hydrogenation rate contains hydrogenation petroleum resin which is not less than 50% of the whole petroleum resin as a binding resin ingredient is indicated by JP,H8-278658,A. In the toner for electrostatic charge image development which adds hydrogenation petroleum resin to the binding resin which contains 5 to 50% of the weight of tetrahydrofuran insoluble matter in JP,H9-222751,A, The toner for electrostatic charge image development whose tetrahydrofuran insoluble matter content of this toner is 1 to 20 % of the weight is indicated. The toner for electrostatic charge image development with which the hydrogenation rate of an ethylenic double bond contains the binder resin for toners which consists of hydrogenation petroleum resin whose not less than 55% or bromination rate is 10g/100 g or less is indicated by JP,H11-52611,A. However, when a picture is formed at high speed, there is a problem that fixing temperature cannot be made low in these toners.

[0004]

In JP,H9-190011,A, the capsule toner for thermal pressure fixing which provided the coat which consists of

hydrophilic resin in the surface of thermoplastics, colorant, the thermally fusible core material in which softening temperature contains hydrogenation petroleum resin 110 ** or less, and its core material is indicated.

However, even if it used the above-mentioned toner as a result of this invention person's examination, when a picture was formed at high speed, it turned out that low temperature fixability is still insufficient.

[0005]

[Problem(s) to be Solved by the Invention]

In spite of being able to establish the purpose of this invention at low temperature, even if it continues under the environment where preservability is good and differs especially at a long period of time and performs durable printing, its transfer nature is good and there is in providing the toner for electrostatic charge image development without the fall of printing density, or generating of fogging.

[0006]

[Means for Solving the Problem]

As a result of inquiring wholeheartedly that this purpose should be attained, by making a coloring particle contain specific hydrogenation petroleum resin, this invention person finds out that the above-mentioned purpose is attained, and came to complete this invention based on this knowledge.

In this way, according to this invention, a toner for electrostatic charge image development which consists of a coloring particle containing polar group content hydrogenation petroleum resin and an external additive is provided.

[0007]

[Embodiment of the Invention]

Hereafter, this invention is explained in full detail.

The toner for electrostatic charge image development of this invention consists of a coloring particle and an external additive.

The coloring particle contains binding resin, colorant, and polar group content hydrogenation petroleum resin, and may contain a charge controlling agent, a release agent, a magnetic material, etc. if needed.

[0008]

as the example of binding resin -- polystyrene, a styrene butyl acrylate copolymer, polyester resin, an epoxy resin, and cyclization -- the resin widely used for the toner from the former, such as polyisoprene rubber, can be mentioned. although the weight average molecular weight in particular of binding resin is not limited -- usually -- 5,000-50,000 -- it is 7,000-30,000 preferably.

[0009]

As colorant, all paints and/or colors besides carbon black, titanium black, magnetic powder, oil black, and a titanium white can be used. As for black carbon black, that whose primary particle diameter is 20-40 nm is used suitably. When particle diameter is in this range, since carbon black can be uniformly distributed in a toner and fogging also decreases, it is desirable.

The quantity of such colorant is usually one to 10 weight section to binding resin 100 weight section.

[0010]

In this invention, polar groups, such as a cyano group, a nitro group, an amino group, and a hydroxyl group, have combined polar group content hydrogenation petroleum resin with the petroleum resin of C5 or C9 grade by which hydrogenation was carried out.

Also in these polar groups, hydrogenation petroleum resin containing a hydroxyl group is preferred. The hydroxyl value of hydroxyl group content hydrogenation petroleum resin is preferred in it being 5 - 250 mgKOH/g, and is more preferred in it being 10 - 220 mgKOH/g.

[0011]

moreover -- the hydrogenation rate in particular of the olefin portion of polar group content hydrogenation petroleum resin is not limited -- usually -- it is not less than 70% still more preferably not less than 50%

preferably not less than 30%. When a hydrogenation rate becomes high, the chromaticity of petroleum resin becomes small and it is 1. Having an adverse effect on the color tone of a toner, when petroleum resin is applied to color toner decreases, and it is 2. A bad smell when it becomes a toner becomes small, and it is 3. The environmental stability of petroleum resin improves and, thereby, the environmental stability of a toner also improves.

the softening temperature of polar group content hydrogenation petroleum resin -- usually -- 70-150 ** 60-200 ** is 80-130 ** still more preferably. If softening temperature is in this range, since the fixability in low temperature and preservability can be combined, it is desirable. Here, softening temperature is the softening temperature by the ring and ball method measured according to JIS K2531.

The weight average molecular weight of polar group content petroleum resin is 200-3,000, and is usually 200-2,000 preferably. weight average molecular weight here dissolves in a tetrahydrofuran -- gel permeation chromatography -- it is fluffy and is a molecular weight of the polystyrene conversion to measure.

Although the chromaticity in particular of polar group content hydrogenation petroleum resin is not limited, it is preferred in Gardner color standards being five or less, and more preferred in it being one or less.

[0012]

As how to obtain this polar group content hydrogenation petroleum resin, it is 1. The method, 2 which carry out hydrogenation of the resin after carrying out the chemical reaction of the compound containing a polar group to petroleum resin in front of hydrogenation and compounding polar group content petroleum resin After carrying out copolymerization of the polymerization nature monomer of isoprene, 1,3-pentadiene, a cyclopentadiene, a dicyclopentadiene, etc. which generates petroleum resin by polymerization, and the polymerization nature monomer which has a polar group and compounding polar group content petroleum resin, the method of carrying out hydrogenation of the resin is mentioned. From the point which is easy to introduce a polar group into resin among these methods to 2 ***** is preferred.

[0013]

The hydroxyl group content hydrogenation petroleum resin preferably used by this invention, i). Under coexistence of a diene system monomer and unsaturated alcohol, use a Friedel-Crafts catalyst and polymerize. ii) thermal polymerization is carried out in autoclave under coexistence of a diene system monomer, the iii diene system monomer which polymerizes under existence of a radical polymerization initiator under coexistence of unsaturated alcohol, and unsaturated alcohol -- what was obtained by carrying out hydrogenation of the hydroxyl group content petroleum resin obtained by the method of ** is preferred.

[0014]

As a diene system monomer used for copolymerization, isoprene, 1,3-pentadiene, a cyclopentadiene, a methylcyclopentadiene, ethylcyclopentadienes and these dimers, trimers, or these ** dimers are mentioned. As unsaturated alcohol, allyl alcohol, clo chill alcohol, 1,4-butenediol, hydroxyethyl acrylate, hydroxyethyl methacrylate, 3-methyl-2-propene-1-ol, 2-methyl-2-propene-1-ol, etc. are mentioned.

Hydroxyl group content petroleum resin is marketed, for example, allyl alcohol denaturation dicyclopentadiene resin, such as Quinton 1700 (made by Nippon Zeon Co., Ltd.) and neo resin NB-90 (made by the Nippon Oil chemicals company), etc. are mentioned.

Hydrogenation of hydroxyl group content petroleum resin can be performed by a publicly known method. For example, using a publicly known hydrogenation catalyst, a hydrogenation pressure is made into the range of about 0.2-30 MPa, reaction temperature is usually made into the range of about 80-350 **, and hydrogenation is carried out. This hydrogenation reaction is performed in the state where usually fused hydroxyl group content petroleum resin, or it dissolved in the solvent. About reaction form, a batch process, circulation types (a fixed-bed type, a fluidized bed, etc.), etc. are not asked.

[0015]

the quantity of polar group content hydrogenation petroleum resin receives binding resin 100 weight section --

usually -- it is five to 20 weight section still more preferably one to 30 weight section preferably 0.5 to 50 weight section. If this polar group content hydrogenation petroleum resin is a core shell type coloring particle which a coloring particle mentions later, containing in a core layer is preferred. An antioxidant, an ultraviolet ray absorbent, etc. may be added to polar group content hydrogenation petroleum resin, and the resin stability and chromaticity may be raised more to it.

[0016]

As a charge controlling agent, the charge controlling agent currently used for the toner from the former can be used. For example, BONTORON N-01 (made by an Orient chemical industry company), the Nigrosine base EX (made by an Orient chemical industry company), SUPIRON black TRH (made by the Hodogaya chemical industry company), T-77 (made by the Hodogaya chemical industry company), BONTORON S-34 (made by an Orient chemical industry company), BONTORON E-81 (made by an Orient chemical industry company), BONTORON E-84 (made by an Orient chemical industry company), COPY CHARGE NX (made by Clariant, LTD.), Charge controlling agents, such as COPY CHARGE NEG (made by Clariant, LTD.), are mentioned, JP,S63-60458,A, JP,H3-175456,A, The 4th class ammonium (salt) group content copolymer according to the description of JP,H3-243954,A, JP,H11-15192,A, etc., The sulfonic acid (salt) group content copolymer according to the description of JP,H1-217464,A, JP,H3-15858,A, etc. can be compounded, and it can also use as a charge controlling agent (henceforth "electrification control resin").

[0017]

Also in these, it is preferred to use electrification control resin. Its compatibility with binding resin is high, and since electrification control resin can obtain the toner which is colorless and where electrostatic property was stabilized also in the color continuous printing in a high speed, it is preferred.

the glass transition temperature of electrification control resin -- usually -- 45-75 ** 40-80 ** is 45-70 ** still more preferably preferably. When glass transition temperature is in this range, the preservability of a toner and fixability can be raised with sufficient balance.

The quantity of a charge controlling agent is usually 0.1 to 10 weight section preferably 0.01 to 20 weight section to binding resin 100 weight section.

[0018]

As a release agent, for example Low molecular weight polyethylene, low molecular weight polypropylene, Polyolefine waxes, such as low-molecular-weight polybutylene; Candelilla, Vegetable system natural wax, such as carnauba, rice, haze wax, and a jojoba; Paraffin, Synthetic waxes, such as petroleum system waxes, such as micro crystalline and PETORO lactam, and a denaturation wax; Fischer Tropsch wax of those; Pentaerythritol tetra Millis Tait, Polyfunctional ester compound [, such as pentaerythritol tetra palmitate and dipentaerythritol hexa Millis Tait,]; etc. are mentioned.

These can be used combining one sort or two sorts or more.

[0019]

A synthetic wax, terminal-modified-polyolefin waxes, a petroleum system wax, a polyfunctional ester compound, etc. are [among these] preferred. In the DSC curve measured with a differential scanning calorimeter also in a polyfunctional ester compound, The endothermic peak temperature at the time of temperature up preferably 30-200 ** 40-160 **, Polyfunctional ester compounds, such as pentaerythritol ester which is in the range of 50-120 ** preferably, and dipentaerythritol ester in the range in which the endothermic peak temperature is 50-80 **, are preferred especially in respect of the fixing-detachability balance as a toner. Also in polyfunctional ester compounds, such as dipentaerythritol ester in the range in which pentaerythritol ester in the range whose endothermic peak temperature at the time of temperature up is 30-200 **, and the endothermic peak temperature are 50-80 **, A molecular weight is 1000 or more, five or more weight sections dissolve at 25 ** to styrene 100 weight section, and since acid value shows an effect remarkable in a fixing temperature fall, the

thing of 10 or less mg/KOH has it. [still more preferred] Endothermic peak temperature is the value measured by ASTM D3418-82.

The quantity of the above-mentioned release agent is usually one to 20 weight section preferably 0.5 to 50 weight section to binding resin 100 weight section.

[0020]

As a magnetic material, for example Magnetite, gamma-iron oxide, a ferrite, Iron oxide, such as an iron overload type ferrite; Iron, cobalt, metal like nickel or these metal, and aluminum, An alloy, its mixture, etc. with metal like cobalt, copper, lead, magnesium, tin, zinc, antimony, beryllium, bismuth, cadmium, calcium, manganese, selenium, titanium, tungsten, and vanadium are mentioned.

[0021]

A coloring particle can be made into the what is called core shell type (or it is also called a "capsule type".) particles obtained combining two polymers which are different in the inside (core layer) and the exterior (shell layer) of particles. By the substance which has softening temperature higher than it covering internal (core layer) low softening point material in core shell type particles, since low-temperature-izing of fixing temperature and the prevention from condensation at the time of preservation can be balanced, it is desirable.

Although the wt. ratio in particular of the core layer of core shell type particles and a shell layer is not limited, it is usually used by 80 / 20 - 99.9/0.1.

By making the rate of a shell layer into the above-mentioned rate, the preservability of a toner and the fixability in low temperature can be combined.

[0022]

0.001-1.0 micrometer of average thickness [0.003-0.5 micrometer of] of the shell layer of core shell type particles is usually preferably considered to be 0.005-0.2 micrometer more preferably. If thickness becomes large, fixability will fall, and when it becomes small, there is a possibility that preservability may fall. No surfaces need to be covered by the shell layer and, as for the core particle which forms core shell type particle toner, a part of surface of the core particle should just be covered by the shell layer.

[0023]

Volume average particle diameter (dv) is 2-20 micrometers, and 3-12 micrometers of coloring particles used for this invention are 4-10 micrometers still more preferably preferably. If particle diameter is small, mobility will fall, transfer nature falls, a skip occurs, and printing density falls. Conversely, if large, fogging and toner scattering will occur and the resolution of a picture will fall.

The particle size distribution (dv/dp) which is the ratios of volume average particle diameter (dv) to number average particle diameters (dp) is 1.0-1.3, and it is still more desirable in it being 1.0-1.2. If particle size distribution is large, a skip will occur, or the fall of transfer nature, printing density, and resolution takes place. Above-mentioned volume average particle diameter and particle size distribution can be made into a mentioned range by classifying, for example.

The volume average particle diameter and particle size distribution of a coloring particle can be measured using a multi-sizer (made by Beckman Coulter) etc., for example.

[0024]

The average degrees of sphericity (Sc/Sr) produced by breaking the area (Sc) of the circle of particles which made maximum length the diameter absolutely by the real project area (Sr) of particles are 1-1.3, and the coloring particle used for this invention is more preferred in it being 1.0-1.2, and still more preferred in it being 1.0-1.15. When an average degree of sphericity becomes larger than 1.3, transfer nature may fall.

This average degree of sphericity can be made into a mentioned range by using a phase inversion emulsification method, a dissolution suspension method, the polymerizing method, etc., for example.

An average degree of sphericity takes the electron microscope photograph of a coloring particle, and here the photograph by Image Processing Division analysis device roux ZEKKUSU IID (made by Nireco Corp.). It is

the value which averaged the degree of sphericity of 100 coloring particles obtained by measuring the area rate of the particles to a frame surface product, and measuring a total processing particle number on 100 conditions a maximum of 2%.

[0025]

The coloring particle in particular that can be used for this invention is not limited by the process, for example, can be obtained by pulverizing method, the phase inversion emulsification method, and the polymerizing method. The coloring particle obtained by the polymerizing method can also be made to meet further. Since the toner which transfer nature and fixability become good and can respond to the image quality of high resolution or improvement in the speed of printing since the coloring particle obtained by the polymerizing method becomes spherical substantially and can distribute hydroxyl group content hydrogenation petroleum resin uniformly in a coloring particle also in these is obtained, it is desirable.

[0026]

Hereafter, the manufacturing method of the coloring particle by the polymerizing method is explained. The coloring particle which constitutes the toner of this invention to the aqueous-dispersion-medium inside of the body containing dispersion stabilizer. After distributing the polymerization nature monomer composition containing the polymerization nature monomer, colorant, and polar group content hydrogenation petroleum resin used as a binding resin ingredient and adding a polymerization initiator, temperature up is carried out to prescribed temperature, and it polymerizes, and it is obtained by drying, after performing washing and drying.

[0027]

As a polymerization nature monomer for obtaining binding resin, a mono- vinyl monomer, a cross-linking monomer, a macro monomer, etc. can be mentioned. This polymerization nature monomer polymerizes and it becomes a binding resin ingredient.

As a mono- vinyl monomer, specifically Styrene, vinyltoluene, aromatic vinyl monomer [, such as alpha-methylstyrene,]; (meta-) -- acrylic acid; (meta-) -- methyl acrylate. (Meta) Ethyl acrylate, acrylic acid (meta) propyl, butyl acrylate (meta), (Meta) 2-ethylhexyl acrylate, acrylic acid (meta) cyclohexyl, (Meta) The derivative of acrylic acid (meta), such as acrylic acid iso BONIRU, acrylic acid (meta) dimethylaminoethyl, and acrylamide (meta); monoolefin monomer [, such as ethylene, propylene, and butylene,]; etc. are mentioned.

A mono- vinyl monomer may be used independently or may be used combining two or more monomers.

Concomitant use with aromatic vinyl monomer independence, an aromatic vinyl monomer, and the derivative of acrylic acid (meta), etc. are suitably used among these mono- vinyl monomers.

[0028]

If a cross-linking monomer and a polymer are used with a mono- vinyl monomer, hot offset will be improved effectively. These cross-linking monomers and a cross-linking polymer are independent, respectively, or can be combined two or more sorts and can be used. Ten or less weight sections of the amount used are usually 0.1 - the amount part of duplexs preferably per mono- vinyl monomer 100 weight section.

If a macro monomer is used with a mono- vinyl monomer, since the balance with fixability in preservability and low temperature will become good, it is desirable. What gives the polymer which has a high glass transition temperature is preferred, and it is independent in the thing especially methacrylic acid ester, or acrylic ester of hydrophilic nature, or what is produced by carrying out copolymerization is more preferred than the glass transition temperature of the polymer produced by polymerizing said mono- vinyl monomer. the amount used receives mono- vinyl monomer 100 weight section -- usually -- it is 0.05 to 1 weight section still more suitably 0.03 to 5 weight section suitably 0.01 to 10 weight section. If the amount of the macro monomer used is in a mentioned range, since preservability will improve with fixability maintained, it is desirable.

[0029]

As dispersion stabilizer, for example Sulfate; barium carbonate, such as barium sulfate and calcium sulfate, Phosphates, such as carbonate; calcium phosphate, such as calcium carbonate and magnesium carbonate; An

aluminum oxide, Metallic compounds, such as metallic-oxides [, such as titanium oxide,], and aluminium hydroxide, Metal hydroxide, such as magnesium hydroxide and a ferric hydroxide; Polyvinyl alcohol, Water soluble polymers, such as methyl cellulose and gelatin; an anionic surface-active agent, a nonionic surface-active agent, an amphoteric surface active agent, etc. can be mentioned, and these may be used independently or may combine two or more kinds.

The dispersion stabilizer containing colloid of metallic compounds, especially metal hydroxide of difficulty water solubility can narrow particle size distribution of a polymer particle, and there is little survivability after washing of dispersion stabilizer, and since it can reproduce a picture vividly, it is [among these] preferred.

[0030]

As for colloid of difficulty water solubility metal hydroxide, in the particle size distribution, it is preferred that particle diameter D_{p90} particle diameter D_{p50} whose number total which measured from the diameter side of a granule is 50% is 0.5 micrometer or less, and is [90] 90% is 1 micrometer or less. If the particle diameter of colloid becomes large, the stability of a polymerization will collapse and the preservability of a toner will fall.

[0031]

Dispersion stabilizer is usually used at a rate of 0.1 to 20 weight section to polymerization nature monomer 100 weight section. Since sufficient polymerization stability is acquired, generation of a polymerization aggregate is controlled and the toner of desired particle diameter can be obtained because this rate is in a mentioned range, it is desirable.

[0032]

As a polymerization initiator, persulfate;4,4'-azobis, such as potassium persulfate and ammonium persulfate (4-cyanovaleric acid), 2,2'-azobis (2-methyl-N-(2-hydroxyethyl) propionamide), 2 and 2'-azobis (2-amidinopropane) dihydrochloride, Azo compounds, such as 2,2'-azobis (2,4-dimethylvaleronitrile) and 2,2'-azobisisobutyronitrile; Di-t-butyl peroxide, JIKUMIRU peroxide, lauroyl peroxide, benzoyl peroxide, T-butylperoxy2-ethylhexanoate, t-hexyl peroxy 2-ethylhexanoate, T-butylperoxy perpivalate, di-isopropyl peroxy dicarbonate, Peroxides, such as di-t-butyl peroxyisophthalate, 1, 1 and 3, and 3-tetramethyl butylperoxy 2-ethylhexanoate and t-butylperoxy isobuthylate, can be illustrated. The redox initiator which combined these polymerization initiators and a reducing agent can be mentioned.

[0033]

It is preferred to choose an oil-soluble meltable polymerization initiator as the polymerization nature monomer also especially meanwhile used, and it can also use a water-soluble polymerization initiator together with this if needed. The above-mentioned polymerization initiator is **** for 0.5 - 10 weight sections still more preferably 0.3 to 15 weight section preferably 0.1 to 20 weight section to polymerization nature monomer 100 weight section.

[0034]

It is preferred to use a regulator when polymerizing. As a regulator, for example t-dodecyl mercaptan, n-dodecyl mercaptan, Mercaptans, such as n-octyl mercaptan and a 2,2,4,6,6-pentamethylheptane-4-thiol; halogenated hydrocarbon [, such as a carbon tetrachloride and carbon tetrabromide,]; etc. can be mentioned. These regulators can be added in the middle of a polymerization before a polymerization start. A regulator is usually preferably used at a rate of 0.1 to 5 weight section 0.01 to 10 weight section to polymerization nature monomer 100 weight section.

[0035]

A polymerization nature monomer, colorant, polar group content hydrogenation petroleum resin, a charge controlling agent, and a release agent are mixed uniformly, using media type dispersion machines, such as a ball mill, as a desirable manufacturing method of a coloring particle, After obtaining a polymerization nature monomer composition, stirring, forming a drop, after adding this constituent to the aqueous-dispersion-medium inside of the

body containing dispersion stabilizer, and adding a polymerization initiator subsequently, using the agitator which carries out a high velocity revolution, agitating speed and time are adjusted so that it may become the particle diameter of a desired coloring particle, and a still smaller drop is formed. Preferably, when forming a drop, temperature is adjusted within the limits of 20-30 **, and it usually performs 10-40 ** of temperature of an aqueous-dispersion-medium object.

Next, while a drop maintains dispersedly stirring of the grade which does not dissociate and sediment, after carrying out temperature up to a predetermined temperature, starting a polymerization and continuing a fixed time polymerization, a reaction is suspended and the water dispersion of a coloring particle is obtained. Then, in order to remove the unreacted polymerization nature monomer which poses a problem of a bad smell from a water dispersion if needed at the time of toner fixing and also to remove the dispersion stabilizer used at the time of a polymerization from a coloring particle, after repeating washing and drying and performing them, a coloring particle is obtained by drying. 40-100 ** of polymerization temperature of a polymerization nature monomer composition is usually 50-90 ** preferably, and polymerization time is 2 to 10 hours preferably for 1 to 20 hours. 20-60 ** of drying temperature is usually 30-50 ** preferably.

[0036]

As a method of manufacturing the core shell type coloring particle which is a desirable coloring particle, methods, such as the spray-drying method, an interface reaction method, an in situ polymerization method, and a phase separation method, are mentioned. Specifically, a core shell type coloring particle is obtained by covering a shell layer to it by making into a core particle the coloring particle obtained by pulverizing method, the polymerizing method, the meeting method, or the phase inversion emulsification method. Also in this manufacturing method, an in situ polymerization method and a phase separation method are preferred from a point of manufacturing efficiency.

[0037]

in Explain the manufacturing method of the core shell type coloring particle by the situ polymerizing method below.

The polymerization nature monomer (polymerization nature monomer for shell) and polymerization initiator for forming shell in the drainage system carrier fluid inside of the body which the core particle is distributing can be added, and a core shell type coloring particle can be obtained by polymerizing.

How to add the polymerization nature monomer for shell to the system of reaction of the polymerization reaction which obtains a core particle and which was performed for accumulating, and polymerize continuously in it as a concrete method of forming shell, Or the core particle obtained by another system of reaction can be taught, and the method of adding the polymerization nature monomer for shell to this, and polymerizing gradually in it, etc. can be mentioned.

[0038]

It is independent, respectively, or two or more sorts of monomers which form a polymer with glass transition temperature of greater than 80 **, such as styrene, acrylonitrile, and methyl methacrylate, as a polymerization nature monomer for shell can be used, combining them.

[0039]

When adding the polymerization nature monomer for shell, since it becomes easy to obtain a core shell type coloring particle to add a water-soluble polymerization initiator, it is desirable. If a water soluble polymerization initiator is added in the case of addition of the polymerization nature monomer for shell, a water soluble polymerization initiator will advance near [where the polymerization nature monomer for shell shifted] the outside surface of a core particle, and it will be thought that it becomes easy to form a polymer (shell) in the core particle surface.

[0040]

As a water soluble polymerization initiator, persulfate;2,2'-azobis, such as potassium persulfate and ammonium

persulfate (2-methyl-N-(2-hydroxyethyl) propionamide), Azo initiators, such as 2,2'-azobis (2-methyl-N-(1,1-bis(hydroxymethyl)ethyl) propionamide), etc. can be mentioned. The quantity of a water soluble polymerization initiator is usually one to 30 weight section preferably 0.1 to 50 weight section to polymerization nature monomer 100 weight section for shell.

[0041]

An inorganic particle and organic resin particles are mentioned as an external additive which constitutes the toner of this invention. These particles added as an external additive have mean particle diameter smaller than particle toner. For example, as an inorganic particle, they are mentioned by silica, an aluminum oxide, titanium oxide, a zinc oxide, tin oxide, barium titanate, strontium titanate, etc., and as organic resin particles, Methacrylate polymer particles, acrylic ester polymer particles, styrene methacrylic-acid-ester copolymer particles, styrene acrylic ester copolymer particles, and a core with a styrene polymer. The core shell type particles etc. in which shell was formed with the methacrylate polymer are mentioned. A silica particle and a titanium oxide particle are preferred, the particles which carried out hydrophobing processing of this surface are [among these] preferred, and especially the silica particle by which hydrophobing processing was carried out is preferred. Although the quantity in particular of an external additive is not limited, it is usually 0.1 to 6 weight section to toner 100 weight section.

[0042]

put the toner of this invention into mixers, such as a Henschel mixer, and it agitates the above-mentioned coloring particle and external additive -- the surface of a coloring particle -- an external additive -- adhesion -- or a part can be made to be able to embed and it can manufacture.

[0043]

the volume specific resistance value (log (ohm-cm)) according [the toner of this invention] to a dielectric loss measuring instrument -- usually -- 10-13 -- it is a thing of 10.5-12.5 preferably. When a volume specific resistance value is small, fogging may occur, and when conversely large, toner scattering, fogging, filming, or cleaning defect may occur.

[0044]

[Example]

Although working example and a comparative example are given to below and this invention is explained to it still more concretely, this invention is not limited only to these working example. A part and % are weight references as long as there is no notice especially.

It evaluated by this example by the following methods.

[0045]

1. Coloring particle characteristic

(1) Volume average particle diameter and particle size distribution

The ratio (dv/dp) with the volume average particle diameter (dv) of a coloring particle and particle size distribution, i.e., volume average particle diameter, and number average particle diameters (dp) was measured by the multi-sizer (made by Beckman Coulter). Measurement by this multi-sizer was performed on diameter:of aperture 100micrometer, the mediumiso ton II, 10% of concentration, and measurement-particles number:100000 piece conditions.

[0046]

2. Toner characteristic

(1) Volume specific resistance value

The volume specific resistance value of the toner put about 3 g of toners into a tablet molding machine 5 cm in diameter, it produced the specimen, having applied about 100 kg of load for 1 minute, and measured it under with the temperature of 30 **, and a frequency of 1 kHz conditions using the dielectric loss measuring instrument (the Ando Electric Co., Ltd. make, kind name "TRS-10 type").

[0047]

(2) Mobility

Three sorts of screens which are 150 micrometers, 75 micrometers, and 45 micrometers respectively are put on this order from a top, and an opening weighs precisely about 4g of toners measured to the top plus sieve, and puts them. Subsequently, after vibrating three sorts of these piled-up screens for 15 seconds on condition of the oscillating intensity graduation 4 using granular material measuring apparatus (the Hosokawa Micron CORP. make, trade name "powder tester"), the weight of the developer which remained in each plus sieve is measured. They are the following formulas 1 about each measured value. **2. And **3. A fluid value is computed by being alike. It measured 3 times per one sample, and the average value was calculated. Formula :

1a=Toner amount (g) of which [(toner weight (g) which remained in the plus sieve of 150 micrometers of openings)/precise weighing was done] x100

2b=Toner amount (g) of which [(toner weight (g) which remained in the plus sieve of 75 micrometers of openings)/precise weighing was done] x100x0.6

3c=Toner amount (g) of which [(toner weight (g) which remained in the plus sieve of 45 micrometers of openings)/precise weighing was done] x100x0.2

Fluid (%) = $100 - (a+b+c)$

[0048]

(3) Preservability

It puts into the container which can seal a toner sample, after sealing, this container is sunk into the constant temperature bath whose temperature is 55 **, after 24 hours pass, it takes out, and it moves so that condensation structure of the toner in a container may not be destroyed to the plus sieve of 42 meshes. Granular material measuring apparatus mentioned above (after setting the intensity of vibration as 4.5 and vibrating for 30 seconds, the weight of the toner which remained on the sieve was measured and was made into the weight of the condensed toner.) From this weight of a toner and weight of a sample that were condensed, the preservability (%) of the weight of the toner was computed. The one where this figure is smaller is highly preservable.

[0049]

3. Image evaluation

(1) Fixing temperature

The printer (24-sheet opportunity) of commercial one ingredient of nonmagnetic development system is converted so that the temperature of a fixing roll part can be changed, the temperature of the fixing roll was changed, by 5 ** unit, the fixing rate of the toner in each temperature was measured, and the fixing examination which asks for the relation between temperature and a fixing rate was done.

Since a fixing rate stabilized the temperature of the changed fixing roll, it was neglected 5 minutes or more, and it was calculated from the ratio of the printing density before and behind tape peeling operation about the solid field of the paper which performed solid printing to the print form and was printed to it with the modified printer after that. That is, image concentration in front of ID and after tape exfoliation was carried out ID back, and the fixing rate computed the image concentration before tape exfoliation from the following formula.

Fixing rate (%) =(after [ID] / before ID) x100

Here, tape peeling operation sticks the adhesive tape mentioned above in the measured part of the examination paper, press it, it is made to adhere in a constant pressure, and is a series of operations of exfoliating adhesive tape in the direction which met paper with constant speed, after that.

In this fixing examination, fixing roll temperature applicable to 80% of a fixing rate was made into the fixing temperature of a toner.

[0050]

(2) Environmental stability

Using the above-mentioned modified printer, under each environment [of H/H environment and the temperature of 10 **, and 20% of humidity] of L/L environment of the temperature of 35 **, and 80% of humidity, The printing density which measured the paper which performed continuous printing by concentration 5% from the first stage, was printed by black solid every 1,000 sheets, and was printed with a Macbeth style reflection density plan or more by 1.3. And fogging of the nonimage area on the photo conductor measured with the whiteness degree plan (made by Nippon Denshoku) counted the continuous printing number of sheets which can maintain 5% or less of image quality, and evaluated the environmental stability of image quality. The last number of sheets printed is 10,000 sheets. As for what is being made or more into 10,000, at least 10,000 sheets show among front that printing density is 1.3 or more, and fogging is 5% or less.

(3) Endurance

The above-mentioned modified printer was also used and the endurance of image quality was evaluated like the above-mentioned environmental stability under the N/N environment of the temperature of 23 **, and 50% of humidity. The last number of sheets printed is 20,000 sheets. As for what is being made or more into 20,000, at least 20,000 sheets show among front that printing density is 1.3 or more, and fogging is 5% or less.

[0051]

(Synthetic example 1)

allyl alcohol denaturation dicyclopentadiene resin (the Nippon Zeon Co., Ltd. make.) Trade name "Quinton 1700" 100 weight section, cyclohexane 100 weight section, and stabilization nickel catalyst (product [made from JGC Chemicals], trade name "N-113") 2.0 weight section were taught to autoclave, and 240 ** was made to react under the high-pressure-hydrogen atmosphere of hydrogen pressure 18MPa for 5 hours. After filtering a catalyst, 220 ** by carrying out distillation under reduced pressure for 0.27kPa 30 minutes, 99% of a hydrogenation rate, 118 ** of softening temperatures, 1 or less (300 Haasen) Gardner of color tones, hydroxyl value 190 mgKOH/g, and hydroxyl group content petroleum resin of the weight average molecular weight 600 (polystyrene reduced property in the GPC method) were obtained.

[0052]

(Working example 1)

80.5 copies of styrene, 19.5 copies of n-butyl acrylate, 0.5 copy of divinylbenzene, and a polymethacrylic-acid-ester macro monomer (the Toagosei chemical industry company make.) the polymerization nature monomer for cores and carbon black (the Mitsubishi Chemical make.) which consist of trade name "AA6" 0.3 copy Trade name "#25B" Seven copies, one copy of electrification control resin (the FUJIKURA KASEI CO., LTD. make, a trade name "FCA-626-NS"; the weight average molecular weight 24,000, glass transition temperature of 60 **), Dipentaerythritol hexa Millis Tait 10 copy, 1.2 copies of t-dodecyl mercaptans, and ten copies of hydroxyl group content hydrogenation petroleum resin obtained in the synthetic example 1 were distributed by the bead mill under the room temperature, and the polymerization nature monomer composition for cores was obtained.

[0053]

On the other hand, it added gradually under stirring of the solution which dissolved 6.2 copies of sodium hydroxide in 50 copies of ion exchange water in the solution which dissolved 10.2 copies of magnesium chlorides in 250 copies of ion exchange water, and the dispersion liquid of magnesium hydroxide colloid were prepared in it. When the particle size distribution of the generated above-mentioned colloid was measured with the SALD particle-size-distribution measuring instrument (made by Shimadzu Corp.), Dp90 whose particle diameter Dp50 whose number total which measured from the diameter side of a granule is 50% is said 90% in 0.35 micrometer was 0.62 micrometer.

On the other hand, two copies of methyl methacrylate and 65 copies of water were micro-disperse--ization-processed with the ultrasonic emulsification machine, and the water dispersion of the polymerization nature monomer for shell was obtained. As for the drop of the polymerization nature monomer for shell, Dp90 was 1.6 micrometers.

[0054]

The polymerization nature monomer composition for cores is fed into the magnesium hydroxide colloidal dispersion liquid obtained by the above, After stirring until a drop is stabilized, and adding five copies of t-butylperoxy2-ethylhexanoate (the Nippon Oil & Fats Co., Ltd. make, trade name "par butyl O") there, it ranks second, The dispersion liquid which made it pass in the total holding time 3 seconds, and passed EBARAMAIRUDA (the Ebara Corp. make, trade name "MDN303V") which rotates at 15,000 rpm were returned and circulated by spray-velocity 0.5 m/s in the original mixing vessel, and the drop of the monomer composition was formed. It adjusted so that an inner nozzle tip might be located in 50 mm under the dispersion-liquid side in a mixing vessel, and the drop was formed by the ten number of times of circulation. The jacket for cooling is attached to the circumference of EBARAMAIRUDA, and about 15 ** cooling water was circulated.

[0055]

One copy of sodium-tetraborate 10 hydrate is added in the magnesium hydroxide colloidal dispersion liquid in which the above-mentioned monomer composition for cores was distributed, and the drop was formed, After putting into the reactor equipped with stirring wings, making a polymerization reaction start at 85 ** and polymerization conversion's reaching to about 100%, 0.3 copy of water-soluble initiator (the Wako Pure Chem make, trade name "VA-086" =2,2'-azobis (2-methyl-N(2-hydroxyethyl)-propionamide)) was dissolved in the water dispersion of said polymerization nature monomer for shell, and it was added to the reactor. After continuing a polymerization for 4 hours, the reaction was suspended and the water dispersion of the core shell type coloring particle was obtained.

Stirring the water dispersion of the coloring particle obtained by the above, sulfuric acid was added, pH was made or less into four, acid cleaning was performed, and filtration separated water. After the repetition line furthermore carried out filtering separation of the solid content for washing and drying several times, the dryer performed 2 day-and-night desiccation at 45 **, volume average particle diameter (dv) obtained 7.8 micrometers, and, in particle size distribution (dv/dp), 1.14 and an average degree of sphericity obtained the core shell type coloring particle of 1.12.

[0056]

To 100 copies of obtained core shell type coloring particles, one copy of silica (the product made by Japanese Aerosil, a trade name "RX100") was added as an external additive, it mixed at the number of rotations of 1400 rpm for 10 minutes to them using the Henschel mixer, and the toner was obtained to them.

The result of the characteristic of the obtained toner and image evaluation is shown in Table 1.

[0057]

(Working example 2)

In working example 1, the coloring particle and the toner were obtained like working example 1 except having changed the addition of hydroxyl group content hydrogenation petroleum resin into three copies. The result of the obtained coloring particle and the characteristic of a toner, and image evaluation is shown in Table 1.

[0058]

(Comparative example 1)

In working example 1, the coloring particle and the toner were obtained like working example 1 except softening temperature having used alicycle fellows saturated hydrocarbon resin (the Arakawa Chemical Industries, Ltd. make, trade name "Al Cong P-115") which is 115 ** instead of the hydroxyl group content hydrogenation petroleum resin A. The result of the obtained coloring particle and the characteristic of a toner, and image evaluation is shown in Table 1.

[0059]

[Table 1]

ID=000002



[0060]

The evaluation result of the toner of Table 1 shows the following things.

The fixability in low temperature is bad, and also the toner of the comparative example 1 which uses the hydrogenation petroleum resin which does not contain the hydroxyl group specified by this invention has bad environmental stability in H/H environment, and its endurance is also bad.

On the other hand, in spite of being able to establish it at low temperature, the toner of this invention has good preservability, does not have deterioration of image quality under different environment, and is understood that endurance is also high.

[0061]

[Effect of the Invention]

According to this invention, in spite of being established at low temperature, even if it continues under the environment where preservability is good and differs especially at a long period of time and performs durable printing, transfer nature is good and the toner for electrostatic charge image development which neither the fall of printing density nor generating of fogging has is provided.

[Translation done.]